NASA Technical Memorandum 106778

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November 1994

National Aeronautics and Space Administration

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SUMMARY

4-Methylpyridinium hydrogen sulfide, $[C_6H_7NH]HS$, M_r = 127.21, consists of $C_6H_7NH^+$ cations and HS^-anions. Z = 2 for the crystal with monoclinic space group *Cm* (#8), dimensions of a = 8.679 (2)Å, b = 7.964 (1)Å and c = 4.860 (2)Å, an angle β of 101.10(2)°, and a volume of V = 329.6(3)Å^3. R = 0.039 and R_w = 0.048 for 385 reflections with $F_o^2 > 3\sigma(F_o^2)$ and 59 variables. Both the $C_6H_7NH^+$ cation and the HS^- anion lie on crystallographic mirror planes with the N,S, two carbon atoms and two hydrogen atoms positioned in the planes. The hydrogen atom of the HS^- anion was not located.

EXPERIMENTAL

The 4-Methylpyridinium hydrogen sulfide, also known as γ-picolinium hydrogen sulfide, was obtained as a by product of the reaction between $GaCl_3$ and thioglycolic acid ($HSCH_2CO_2H$) in a γ-picoline solution. The specifics of the reaction, which was carried out under an argon atmosphere, are as follows. 2.0mL (28.7mmol) of $HSCH_2CO_2H$ was slowly added to a solution of 0.87g of $GaCl_3$ in 30mL of γ-picoline. After reacting for 24 hours, the precipitate which formed was removed by filtration. The filtrate solution was layered with 30mL of freshly distilled hexanes. This produced colorless crystals of the 4-methylpyridinium hydrogen sulfide which were allowed 80 days to grow. The crystals were then collected, washed with three 10mL aliquots of hexanes and dried in vacuo.

A 0.47×0.32×0.22mm crystal was sealed in a glass capillary and mounted on an Enraf-Nonius CAD-4 automated diffractometer which utilizes Mo Kα radiation of wavelength λ = 0.71073Å . Cell constants were determined from least-squares refinement of 25 reflections in the range $18 < \theta < 23°$. Intensity data were collected using the ω-2θ scan technique in the range $4 < 2\theta < 55°$ at a temperature of 20 °C. The scan rate varied from 2 to 16° min^{-1} with ω-scan width = (0.74 + 0.350tanθ). Intensities were corrected for Lorentz and polarization effects. Absorption effects were corrected based on the empirical method of Walker & Stuart (ref. 12) with T_{min} = 0.421 and T_{max} = 1.000. 413 unique reflections were collected in the index ranges $0 \le h \le 11$, $0 \le k \le 10$, and $-6 \le l \le 6$. Of these unique reflections, the 385 whose intensities fit $F_o^2 > 3\sigma(F_o^2)$ were used in the refinements. The structure was solved using the structure solution program SHELX-86 (ref. 10). The remaining atoms were located in succeeding difference Fourier syntheses. With the exception of the hydrogen

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atom of the HS^- ion, hydrogen atoms were located and their positions and isotropic thermal parameters were refined. The structure was refined in full-matrix least squares. The function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight, w, defined by the Killean and Lawrence (ref. 8) method with terms of 0.020 and 0.1. The final refinement parameters are $R = 0.039$, $R_w = 0.048$, $S = 1.617$ and $(\Delta/\sigma)_{max} = 0.02$. The maximum residual peak in the final difference Fourier map was 0.25 $e\text{Å}^{-3}$. Atomic scattering factors were taken from reference 3. Anomalous dispersion effects were included in F_c (ref. 6) and the values of f' and f'' were those of reference 4. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$, and various classes of indeces showed no unusual trends. All calculations were performed on a VAX computer. Refinement was done using Enraf-Nonius *MolEN* (ref. 5). Table I* lists final positional and equivalent isotropic thermal parameters. Bond distances and angles are listed in Table II. The *ORTEP* (ref. 7) drawing in Figure 1 shows the stereochemistry of the molecule.

RELATED LITERATURE

X-Ray structural characterizations of 4-methylpyridinium bromide (ref. 2) and piperidinium hydrogen sulfide (refs. 1 and 11). ^1H NMR spectrum and viscosity and conductance measurements of 4-methylpyridinium bromide (ref. 9).

MTA gratefully acknowledges a postdoctoral fellowship from the National Research Council - NASA Lewis Research Center. AFH acknowledges support from the Director's Discretionary Fund at NASA Lewis. SAD acknowledges partial support from NASA grant NCC3-162. EMG acknowledges support from NASA grant NCC3-281.

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*Lists of structure factors, anisotropic thermal parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH 1 2HU, England.

TABLE I.—POSITIONAL AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS WITH e.s.d's IN PARENTHESES

$$B_{eq} = (1/3)\sum_i \sum_j B_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	B_{eq}(Å^2)
S	0.16570	1.	0.95320	3.86(2)
N	0.4327(5)	1.	0.6516(9)	3.61(8)
C(2)	0.4863(5)	0.8540(5)	0.5731(9)	3.93(7)
C(3)	0.5969(5)	0.8508(5)	0.4101(8)	3.72(6)
C(4)	0.6555(6)	1.	0.323(1)	3.23(8)
C(7)	0.7805(7)	1.	0.152(1)	4.8(1)
H(1)	0.349(9)	1.	0.77(2)	6(2)*
H(21)	0.459(7)	0.756(9)	0.68(1)	8(2)*
H(31)	0.632(8)	0.754(9)	0.35(1)	9(2)*
H(71)	0.872(9)	1.	0.30(2)	6(2)*
H(72)	0.77(1)	0.89(1)	0.01(2)	12(2)*

*Refined with istoropic B's.

TABLE II

[Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses.]

S-H(1)	1.98(9)	C(3)-C(4)	1.390(5)
N-C(2)	1.335(5)	C(3)-H(31)	0.90(8)
N-H(1)	1.00(9)	C(4)-C(7)	1.488(8)
C(2)-C(3)	1.357(7)	C(7)-H(71)	1.0(1)
C(2)-H(21)	0.98(8)	C(7)-H(72)	1.1(1)
C(2)-N-C(2)	121.1(6)	C(3)-C(4)-C(7)	121.2(3)
C(2)-N-H(1)	119.4(3)	C(4)-C(7)-H(71)	99(6)
N-C(2)-C(3)	120.5(4)	C(4)-C(7)-H(72)	113(5)
N-C(2)-H(21)	114(4)	C(4)-C(7)-H(72)	113(5)
C(3)-C(2)-H(21)	124(4)	H(71)-C(7)-H(72)	115(6)
C(2)-C(3)-C(4)	120.2(4)	H(71)-C(7)-H(72)	115(6)
C(2)-C-(3)-H(31)	121(5)	H(72)-C(7)-H(72)	103(11)
C(4)-C(3)-H(31)	118(5)	S-H(1)-N	173(8)
C(3)-C(4)-C(3)	117.5(5)		

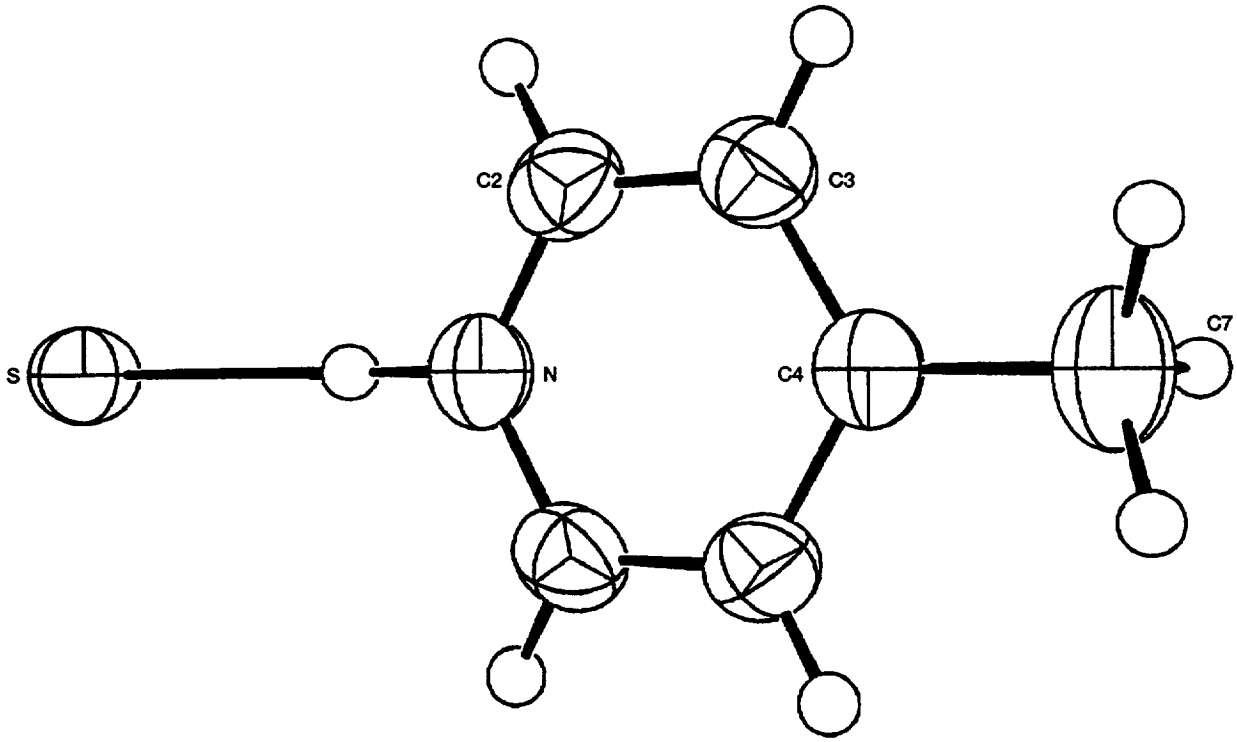

Figure 1.—ORTEP (Johnson, 1965) drawing of the $[C_6H_7NH][HS]$ molecule (without the undetected H of HS^-) showing the atomic-labeling scheme. Thermal ellipsoids are drawn at the 50% probability level while isotropic hydrogen thermal parameters are represented by spheres of arbitrary size.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (*Leave blank*)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	November 1994	Technical Memorandum

4. TITLE AND SUBTITLE

Structure of 4–Methylpyridinium Hydrogen Sulfide

5. FUNDING NUMBERS

WU–233–01–0A

6. AUTHOR(S)

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135–3191

8. PERFORMING ORGANIZATION REPORT NUMBER

E–9231

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Washington, D.C. 20546–0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

NASA TM–106778

11. SUPPLEMENTARY NOTES

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12a. DISTRIBUTION/AVAILABILITY STATEMENT

Unclassified - Unlimited
Subject Category 25

12b. DISTRIBUTION CODE

13. ABSTRACT ***(Maximum 200 words)***

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14. SUBJECT TERMS

X-rays; Crystal; Pyridines; Nitrogen compounds, Hydrogen sulfide

15. NUMBER OF PAGES

6

16. PRICE CODE

A02

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	